

COLOUR AND CHEMICAL CONSTITUTION.

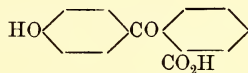
PART II.—THE SPECTRA OF THE MIXED PHTHALEINS AND OF THE
SULPHONE-PHTHALEINS.

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In the first part of this paper (read March 21, 1917; sent in January 18th) an attempt was made to discover the laws which govern the colour of organic dye-stuffs by choosing one of such simple constitution and easy manufacture that it was not a troublesome matter to prepare and examine a large number (over fifty) of derivatives of the parent substance, and thus solve, to a large extent, the problem of the effect on colour of varying the substituting groups—without wasting a lifetime in the preparation of the necessary compounds.

Phenolphthalein is a quasi-symmetrical compound, since it contains two equal $-\text{C}_6\text{H}_4\text{OH}$ groups, and the same is true of about forty of the compounds described in Part I; but in addition a number of compounds were described which have $-\text{C}_6\text{H}_5$ plus $-\text{C}_6\text{H}_4\text{OH}$, and are thus mixed phthaleins of a kind, although not dibasic like the true phthaleins. They were made by condensing benzoylbenzoic acid with phenols.

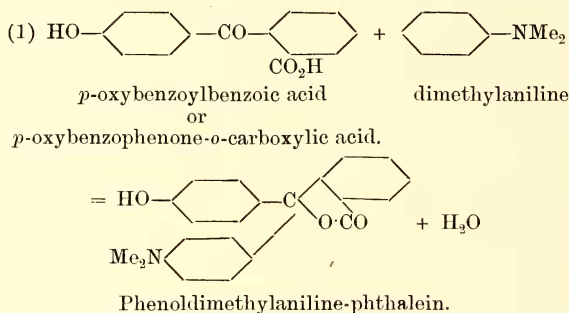
In April of this year (1917) it struck me that substituted benzoyl-benzoic acids, particularly



(which is easily made from phenolphthaleinoxime), might be used to make true dibasic mixed phthaleins containing one $-\text{C}_6\text{H}_4\text{OH}$ group as well as the residue of another phenol $-\text{C}_6\text{H}_{4-n}\text{X}_n\text{OH}$.

On trying the experiments I found that the above-mentioned *p*-oxy-benzoyl-*o*-benzoic acid is capable of combining with all sorts of phenols with the utmost ease; in most cases simple boiling of a mixture of the ingredients without a condensing agent for ten seconds suffices to give a good yield of the desired mixed phthalein. In addition, the acid can combine with the most unexpected aromatic substances (phenol-esters, anhydrides, and amines, whether free or substituted in the nitrogen) to

yield mixed phthaleins of a new type, although phthalic anhydride does not condense with these substances. Thus coumarine, quinosol, dimethylaniline, and to some extent even menthol, yield phthaleins with this acid; in fact, probably any ring compound with $-\text{OH}$ or $-\text{NH}_2$, either free or substituted, will react in this way, provided that it has a free *para*- or *ortho*-position. The following scheme represents the combination in the simpler of the two cases, the *para*-position being the preferred one:



Unfortunately for my priority, the principle of this synthesis has in the meantime been discovered independently in the United States, Messrs. Orndorff and Murray ('Journ. Amer. Chem. Soc.' April, 1917) having published the preparation of several of my mixed phthaleins and thus evidently anticipated me by a few months. They did not, however, "spectroscopically" their compounds.

Table I gives the results of my investigation.

It may be noted that (1) phenolcoumarinphthalein is a direct derivative of ordinary phenolphthalein, being its *o*-acrylic acid compound, the acrylic group $-\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ having practically the same effect on the colour as a methyl group; (2) quinosol is 8-oxyquinoline, *i.e.* with the $-\text{OH}$ group in a different ring from the nitrogen; the pyridine ring has less effect on the colour than the benzene-ring, comparing the quinosol- with the α -naphthol- compound; (3) the hydrogenated rings of menthol and tetrahydronaphthol have much less effect than the corresponding thymol and naphthol rings, but owing to one attachment of the tetrahydronaphthol ring being *meta* to the $-\text{OH}$ (see Part I), the effect is greater than that of a powerful group (*e.g.* $-\text{OCH}_3$) in the *ortho*-position; (4) the effect of the phenolic $-\text{OH}$ having to take up the *ortho*-instead of the usual *para*-position to the central carbon is a greatly increased shift of the colour or lowering of frequency, *e.g.* the β -naphthol derivative.

It is probable that the absorption-band of di- β -naphtholphthalein (from β -naphthol and phthalic anhydride) is right off the visible spectrum, which accounts for it not having been recognised.

The mixed aminophthaleins are remarkably sensitive to excess alkali,

which easily bleaches their colour; otherwise from their brilliant colours they would make excellent indicators.

TABLE I.
Spectra of the Dibasic Mixed Phthaleins.

No.	Name.	Colour in Alkali.	Wave-length of Absorption Band.	Percentage Difference from Phenolphthalein.	Wave-length in conc. H ₂ SO ₄ .
1	Phenolthymolphthalein .	Purple	578	4.1	About 520
2	Phenolorthocresolphthalein	Pink	563	1.5	
3	Phenolguaiacolphthalein .	Purple	580	4.4	About 525
4	Phenolcarvacrolphthalein .	"	580	4.4	
5	Phenol- α -naphtholphthalein	Indigo	607*	8.7	566 and violet.
6	Phenol- β -naphtholphthalein	Green	637*	13.0	
7	Phenolresorcinolphthalein (mixture of two)	Dichroic-red	558 and 494	Abnormal	503
8	Phenolphloroglucinolphthalein (mixture of two)	Dichroic-red	550 and 490	"	nil.
9	Phenolpyrogallolphthalein (mixture of two)	Dichroic-red	580 and 480	"	"
10	Phenolpyrocatecholphthalein	Purple	579	4.3	522
11	Phenolcoumarinphthalein .	Pink	565 (slight fluorescence)	1.9	
12	Phenolquinosolphthalein .	Blue	598	7.3	520
13	Phenolmentholphthalein .	Pink	About 563	1½	
14	Phenoltetrahydro- α -naphtholphthalein	Blue-purple	588	5.8	530
15	Phenolanilinephthalein .	Pink	558	0.7	Ultra-violet.
16	Phenolmonomethylaniline-phthalein	Red-purple	576	3.8	"
17	Phenoldimethylaniline-phthalein	Blue-purple	587½	5.6	"
18	Phenol- α -naphthylamine-phthalein	Yellow-green	About 740* (fluorescent)	25	

* Plus ultra-violet.

In any case the easy reaction of all these organic compounds with oxybenzoylbenzoic acid affords a simple analytical test for phenols and amines, the position of the absorption band in the spectrum at once indicating what the phenol (or amine) used was.

If a numerical comparison be made between the spectra of any one of these mixed phthaleins and the corresponding ordinary phthalein, the remarkable discovery is made that the mixed phthalein spectrum is not quite intermediate between those of phenolphthalein and the other phthalein. Thus di-phenolphthalein (ordinary phenolphthalein) has λ 554, phenolthymolphthalein has λ 578, and di-thymolphthalein has λ 597. In other words, the entrance of one pair of methyl and isopropyl groups depresses the

frequency of vibration by 4.1 per cent., and the entrance of a second pair only brings the depression to 7.2 per cent. The same law is true of all the others, and may be stated as follows—that the entrance of the first grouping causes a change equal to about 58 per cent. of the total change due to two groupings.

This phenomenon is easily explained in terms of the interference of the rings, or rather of their projecting substituents, with one another (see Part I). It is obvious that the entrance of one —OCH_3 group into one ring of phenolphthalein will cause a great interference with the other empty ring and that the entrance of —OCH_3 into the other ring will cause a second interference, but not so great.

THE SULPHONE-PHTHALEINS (SO-CALLED SULPHUREINS).

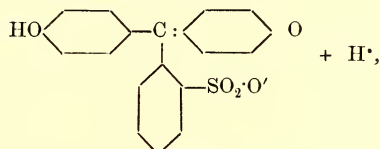
I have discovered that some of these can be easily made by heating phenols with “saccharin” (the artificial sweetening agent) and a little sulphuric acid, followed by boiling the product with dilute acid to split off ammonia. They form excellent indicators. In my opinion, phenolsulphonephthalein is the best general indicator yet discovered for sensitiveness and definiteness of colour. Its constitution is that of phenolphthalein with the group CO replaced by SO_2 ; it is therefore, chemically speaking, the ortho-sulphonic acid of benzaurine (see Part I). The following table gives the spectra of those examined so far.

TABLE II.

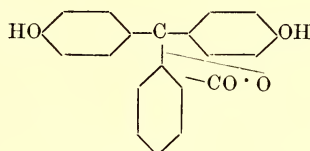
No.	Name.	Colour in Alkali.	Wave-length absorbed in Alkali.	Wave-length absorbed in <i>N</i> HCl.	Wave-length absorbed in conc. H_2SO_4 .
1	Phenolsulphonephthalein .	Purple-pink	563	507	500 (practically same as phenolphthalein).
2	Thymolsulphonephthalein	Blue	604	?	About 570
3	α -naphtholsulphonephthalein	Olive-green	About 730	?	About 720 and 500
4	Guaiacolsulphonephthalein	Blue	608	565	570
5	Resorcinolsulphonephthalein	Salmon (fluorescent)	497 (and 522 faint)	576	(<i>Cf.</i> fluorescein).

In all these cases the *neutral* colour is a shade of yellow or brown, not colourless as in the case of the ordinary phthaleins, but none of them when neutral gives a spectrum containing an absorption band; loss of more or less of the violet is all that can be observed. No satisfactory explanation of this *coloured* neutral phase of the sulphonephthaleins has yet been put

forward, but it is probably due to the high ionisation of the $-\text{SO}_3\text{H}$ group as compared with the $-\text{CO}_2\text{H}$ group in the ordinary phthaleins. Thus neutral phenol-sulphonephthalein is probably

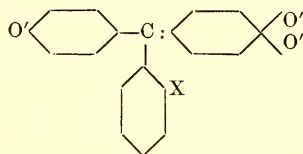


i. e. a substance which is still quinonoid; whereas neutral phenolphthalein is a non-quinonoid lactone, viz.:



and it should be remembered that neutral benzaurine, the parent substance of both, is yellow, like the sulphonephthalein.

It is therefore probable that the deeply coloured *alkaline* solutions of all the phthaleins of every class have the same sort of constitution and one *different* from the above, viz.:



where X is either H, or CO_2' , or SO_3' .

This is the only theory of phthalein colour which explains all cases, including those in which there is only one phenolic ring, such as monoxydiphenylphthalide and phenol-phthalein-monomethyl ether.

As regards the difference in alkaline colour between any phthalein and the corresponding sulphone-phthalein, it will be seen from the table that the change of CO into SO_2 makes little difference, the frequency of the absorption-band being lowered by about $1\frac{1}{2}$ per cent., which is about the same difference as is produced by the entrance of one ortho-methyl group into ordinary phenolphthalein to form phenolcresolphthalein.

OTHER NEW PHTHALEINS AND THEIR SPECTRA.

These were made from 3-nitrophthalic acid (itself made from α -nitronaphthalene).

A table giving the position of their absorption bands is appended:

TABLE III.

No.	Name.	Colour in Alkali.	Wave-length of Absorption Band.	
1	Phenol-3'-nitrophthalein .	Pink	559	Easily bleached by excess alkali.
2	Thymol-3'-nitrophthalein .	Blue	602	Easily bleached by excess alkali.
3	Resorcinol-3'-nitrophtha- lein	Salmon (green fluorescence)	495	(= 3'-nitrofluores- cein).
4	α -naphthol-3'-nitrophtha- lein	Brown (blue fluorescence)	About 730	—

The 3'-nitro-group has thus quite a small effect, quite different from that of nitro-groups in the phenol rings.

In addition, resorcinol-3'-oxyphthalein (3'-oxyfluorescein) has been made from 3-oxyphthalic acid. Its absorption-band wave-length is λ 489.

Resorcin-saccharein, which is fluorescein with SO_2NH instead of $\text{CO}\cdot\text{O}$, is identical in appearance and spectrum with fluorescein.